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Evaluation of the Effects of Microclimate Differences on Corrosion

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16. ABSTRACT

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Relative humidity was found to be the most important but least accurate variable. Because it is seldom measured at exposure sites, an equation was developed to relate site to site relative humidity differences to temperature differences. With average relative humidity and another empirical equation, time-of-wetness can be estimated. The results are in good agreement with time-of-wetness from the ACMs.

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F. H. Haynie[1]

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ABSTRACT: Analytical and statistical analyses of data obtained from a contracted exposure study performed by Rockwell International in St. Louis, Mo. reveal that many microclimate differences can account for observed differences in corrosion behavior within a geographic region. Data from Mansfeld's Atmospheric Corrosion Monitors (ACM's) were evaluated with data from the Regional Air Monitoring System (RAMS). Relative humidity, temperature, wind speed, and levels of total sulfur gases such as sulfur dioxide and oxides of nitrogen were found to be statistically significant variables. Problems of covariance were avoided by partitioning the large data set into subsets.

Relative humidity was found to be the most important but least accurate variable. Because it is seldom measured at exposure sites, an equation was developed to relate site-to-site relative humidity differences to temperature differences. With average relative humidity and another empirical equation, time-of-wetness can be estimated. The results are in good agreement with time-of-wetness from the ACM's.

KEY WORDS: atmospheric corrosion, climate, pollution, measurement, statistical analysis, zinc, steel, wind speed, temperature, relative humidity, time-of-wetness, sulfur dioxide, nitrogen oxide

In 1974 the Environmental Protection Agency (EPA), through Rockwell International as a prime contractor, established a Regional Air Monitoring System (RAMS) to develop and validate regional air quality simulation models. This 25-station network in the St. Louis, Mo. area was one of the most sophisticated of its type. Data from continuous gaseous air pollution monitors and meteorological sensors were recorded in a central computer. Considerable effort was devoted to assuring the quality of the data [*1*].[2]

Other types of studies were done in the St. Louis area to take advantage of this unique system. Among them was a study of the effects of pollutants on materials [*2*]. Materials were exposed for periods of from 3 to 30 months and were evaluated for cumulative damage after exposure. The establishment

[1] Environmental Sciences Research Laboratory, EPA, Research Triangle Park, NC

[2] The italic numbers in brackets refer to the list of references appended to this paper.

of relationships between damage and environmental conditions was limited to multiple regression of the damage values with long-term averages of the RAMS data [*2*].

Although long-term averages of collected data have a much higher probability of being closer to a true mean than do individual values or short-term averages, there are disadvantages in using them to analyze for functional relationships. There can be bias in validation procedures that preclude certain types of suspect data. More important, the number and range of values are drastically reduced.

In 1976, continuous Atmospheric Corrosion Monitors (ACM's) were placed at four sites and the data from these devices were continuously recorded in the central computer. These monitors were galvanic cells of copper/zinc and copper/steel as described by Mansfeld [*3*]. The output from the instrumentation to the computer was a voltage proportional to the logarithm of the measured cell current. For the fall of 1976, a period when the RAMS data were considered to be most valid, a data tape of hourly averages of the ACM outputs was created. These values are proportional to the geometric mean of the cell current. Hourly averages of the continuously monitored RAMS data that have been subjected to several stages of validation are on file. Combining these data creates a file of over 2000 sets having a much wider range of values than do long-term averages.

This paper analyzes this set of data to associate corrosion behavior with observed microclimate differences at the four sites and the changes in microclimates with time.

Validation and Treatment of Data Types

Multiple-regression analysis techniques are based on the assumptions that "independent" variables are fixed and not covariant. In essence, the values upon which the dependent variables are regressed are assumed to be error-free and not related to each other. In the real world of meteorological and pollution data, neither of these assumptions is true. Thus, it is prudent to analyze each data type independently to determine the relative magnitude and causes of error, then analyze for covariance before multiple-regression analysis is performed. Also, the recorded data for each type need to be converted to units that make scientific as well as mathematical sense in a statistical relationship.

There are three basic types of data in this set: (1) ACM response, (2) meteorological data, and (3) gaseous pollution data. Each of these types will be discussed separately.

ACM Response

ACM's consisting of galvanic cells of alternating plates of copper and zinc separated by sheets of plastic insulators were exposed to the atmosphere at Sites 103 and 106 within the urban area of St. Louis. When an electrolyte

bridges the exposed plate edges, the galvanic potential between the copper and zinc creates a current. The amount of current is a function of the amount and type of electrolyte on the surface, as well as other factors.

Similar ACM's of copper and steel were exposed at Sites 112 and 122. Site 112 is within the beltline of St. Louis but up prevailing wind from the center of the city. Site 122 is approximately 40 km north of center city.

The instrumentation at each site was such that a logarithmic conversion of the current produced a 1-V change in output for each decade change in current. With a positive 2-V offset to prevent the recording of negative numbers, the output of the instrumentation at μA current was 2 V (Fig. 1).

Figure 1 shows histograms of the recorded data for the four sites. At each site there appears to be a bimodal distribution of values: one large mode at the low end for a dry surface, and the other small one at the high end for a com-

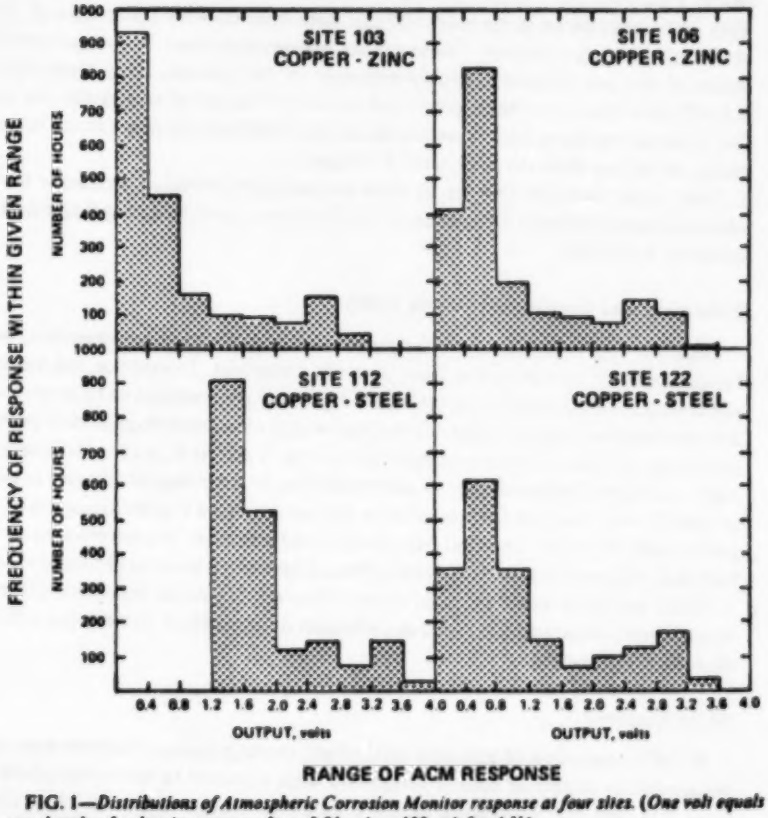

FIG. 1—*Distributions of Atmospheric Corrosion Monitor response at four sites. (One volt equals one decade of galvanic current—from 0.01 μA to 100 μA for 4 V.)*

pletely wet surface. The current measured when the surface of the ACM is dry is due to the background current of the ACM amplifiers. The current at the high end is the result of galvanic corrosion. In between the two modes, the current measures corrosion related to the moisture on the ACM surface.

The background current has a much higher value at Site 112 than for the other three sites. The values of the upper modes that are associated with corrosion are more comparable between sites and types of ACM's. Because corrosion is the parameter to be studied, the background current must be subtracted from the total current to get corrosion currents.

The most obvious response of the ACM's is to changes in relative humidity. When the ambient relative humidity is low and not changing, the measured current should be the background current. The mass and geometry of the ACM's are such that the response may lead or lag ambient changes. For example, moisture collected on the surface takes time to evaporate after there has been a lowering of the ambient relative humidity. It is, thus, possible to have the surface wet with a corrosion current being generated at the same time that the ambient relative humidity is relatively low. In addition, as will be discussed later, the determination of relative humidity is subject to considerable error.

Three different techniques were used to calculate background current: (1) average of values around the lower mode, (2) average of values occurring at relative humidities below 40 percent, and (3) the zero intercept of a linear regression of current on relative humidities below 50 percent. A conversion of these data to equivalent corrosion rates for zinc and steel was made using the following factors: (1) exposed areas of zinc and steel, respectively, of 4.3 and 3.5 cm^2, and (2) respective conversion factors (from electrochemical equivalence) of 14.96 and 11.62 μm/year for each $\mu A/cm^2$ measured on zinc and steel. The converted results are presented in Table 1.

With the exception of Site 112, all of the values are small and relatively consistent. Even Site 112 is small when compared with upper-mode values.

The regression intercepts were taken as background current to calculate a baseline for zero corrosion. The measured current above these values was converted to corrosion rates for each hour at each site. In Table 2, averages of these data for the entire exposure period are compared with corrosion rates calculated from weight loss data for weathering steel and galvanized steel

TABLE 1—*Background current as corrosion rate, μm/year.*

Site	Mode Avg	Avg Below 40 RH	RH Regression Intercept
103	0.073	0.077	0.056
106	0.087	0.097	0.080
112	1.084	1.403	1.518
122	0.082	0.082	0.051

TABLE 2—*Comparison of calculated corrosion rates.*

		Corrosion Rates, μm/year		
			Weight Loss	
Site	Metal	ACM	Mean	Standard Deviation
103	zinc	2.146	0.655	0.028
106	zinc	3.236	0.738	0.014
112	steel	10.992	3.607	0.541
122	steel	5.221	7.852	0.767

over the same period [*2*]. These values are consistent considering the differences between materials and geometry of specimens.

ACM response has been used to estimate time-of-wetness. Because the response is a continuum of values between two modes rather than two values, time-of-wetness must be defined with respect to some value in between the two modes. The surface is considered wet when the selected value is exceeded. The value should be high enough so as not to be influenced by error in the background or leakage current, yet low enough to account for most of the corrosion. Table 3 shows how percentages of corrosion and time above a stated value of corrosion rate vary with that value for the four sites. At Site 103, for example, 91.1 percent of the corrosion occurs when the corrosion rate exceeds 0.5 μm/year. That corrosion rate is exceeded only 23.5 percent of the time. Below a corrosion rate of 1.5 μm/year the percentage of time increases disproportional to the increases in percentages of corrosion. This is an indication of the distribution of values around the background current mode. Above a corrosion rate of 1.5 μm/year, values are not appreciably affected by variations in background current and the ACM's are considered to be wet. Based on regressions of data in Table 3, best estimates of the percentage of time the surfaces of the ACM's were wet are presented in Table 4.

These data in Table 4 show that not only is the difference between steel and zinc ACM's highly significant, but also that the differences between sites are statistically significant. These results are indicative of environmental differences and differences in hygroscopicity of corrosion products on the surfaces formed at different test sites.

Meteorological Data

Of several types of meteorological data recorded at each site, three are believed to significantly affect the corrosion rate at any given time. These three are (1) wind speed, (2) temperature, and (3) dew point.

Wind Speed—Wind speed was measured at the top of 30-m towers at each of the four sites. The materials including the ACM's were exposed at approximately 3 m from the ground. The flux of reactants to the ACM surface is

TABLE 3—*Percent of corrosion and time when stated corrosion rate is exceeded.*

Corrosion Rate, μm/year	Site 103		Site 106		Site 112		Site 122	
	Corrosion	Time	Corrosion	Time	Corrosion	Time	Corrosion	Time
0.5	91.1	23.5	94.5	25.9	99.8	34.2	96.8	31.2
1.0	89.8	19.9	93.6	21.9	99.4	29.3	96.1	26.3
1.5	88.5	17.7	92.9	20.0	99.1	26.9	95.5	23.9
2.0	87.5	16.4	92.1	18.4	99.0	25.8	95.2	22.9
2.5	86.1	15.1	91.4	17.4	98.8	24.9	94.9	22.2
3.0	84.9	14.2	90.7	16.8	98.5	23.8	94.6	21.6

TABLE 4—*Percent of time when wet.*

Site	ACM	Best Estimate	Standard Deviation
103	cu/zn	18.42	0.29
106	cu/zn	20.69	0.40
112	cu/steel	28.21	0.54
122	cu/steel	25.33	0.61

controlled by turbulent diffusion. The magnitude of eddy diffusion is related to the wind shear at the ACM surface. The wind shear at the ACM is a function of the wind speed at the level of the ACM, which in turn is a function of the wind speed at 30 m.

From theoretical considerations [*4*] it is assumed that wind velocity variation with height from the ground and distance from the ACM obeys the relationship

$$v^* = 3.8 + \frac{1}{3.6} \ln S^* \tag{1}$$

where

$$v^* = \frac{v}{v^*} \text{ and } S^* = \frac{v^* S}{\nu}$$

and

v = wind velocity,
v^* = "friction velocity" = $\sqrt{\tau/\rho}$,
S = height,
ν = kinematic viscosity,
τ = shear, and
ρ = density.

Based on an analogy between mass and momentum transfer in turbulent flow [*5*], the deposition velocity may be expressed as

$$u = \frac{v^{*2}}{v} \tag{2}$$

where

u = deposition velocity,
v = wind speed near ACM, and
v^* = friction velocity near ACM.

With Eq 1, the wind velocity at a height of 30 m, and a kinematic viscosity for air of 0.15 cm^2/s, the friction velocity can be determined and subsequently the wind speed near the ACM. Assuming a distance of 10 cm from the ACM,

the friction velocity near the specimen and the deposition velocity can be calculated.

The form of the equation requires a trial-and-error solution. This was done for a range of wind speed values and the results were fitted to the following empirical equation

$$u = 0.3025\,[v - 0.1875v^{0.8275}]^{0.754} \tag{3}$$

where u is the deposition velocity in centimetres per second and v the wind speed at a height of 30 m in metres per second. Deposition velocity (u) is possibly an important factor affecting corrosion rate because pollutant flux is equal to the deposition velocity times the pollutant concentration.

Calculated values of u using Eq 3 and the RAMS data for wind speed range between 0.12 and 1.4 cm/s with most values between 0.3 and 1.0 cm/s. The averages of deposition velocity ranged from 0.504 cm/s at Site 122 to 0.787 cm/s at Site 103. These theoretically calculated values are consistent with experimentally determined values for gaseous pollutants [6].

Temperature—The ambient temperature data were most likely the most reliable of any of the measured variables. The instrumentation accuracy was ±0.05 deg C and, based on comparisons of the number of missing hourly averages after validation, the temperature instruments were the most reliable of all the instruments used at the RAMS sites. The fraction of valid hourly averages ranged from 0.9848 at Site 122 to 0.9995 at Site 103.

The data consist of minute averages of 120 half-second data readings. These minute averages were transmitted to the central computer for validation, storage, and hourly averaging.

Temperature affects corrosion rate through changes in kinetics and through changes in relative humidity which alter time-of-wetness. The effect on kinetics is expected to have an Arrhenius behavior and for that reason the temperature values were inverted using the relationship

$$E = \frac{1000}{T + 273.16} \tag{4}$$

where E is desired temperature parameter and T the hourly average temperature in degrees Celsius. The logarithm of the corrosion rate is expected to be linearly related to the negative of this parameter.

Dew Point—While the temperature data were the best of the RAMS data, the dew-point data were probably the worst. The claimed accuracy of the instrument was ±1 deg C. The instruments were very unreliable because of the accumulation of contaminants and moisture on the mirror used to sense dew formation. An attempt was made to eliminate this problem by drastically reducing the operating and sampling time. The instruments were operated for 5 min out of each 1/2 h. Thus, hourly averages consist of no more than averages of two sets of 5-min averages.

The validation procedure, although conceptually sound, created a highly

undesirable bias in the hourly averages. Data were rejected if the dew point exceeded the temperature by more than 1 deg C. This behavior is most likely to occur when the relative humidity is near its maximum. Thus, rejecting these data unrealistically lowers the average dew point. The percent of hourly average data thus validated is 85, 87, 85, and 98, for Sites 103, 106, 112, and 122, respectively.

Relative humidity as a proxy for time-of-wetness is the most important variable affecting atmospheric corrosion. In order to properly evaluate the effects of any other variables, the effects of relative humidity must be understood.

An empirical relationship for relative humidity as a function of temperature and dew point was obtained by curve-fitting table data [7]. The relationship is

$$RH = 100\, e^{-(5.3837 - 0.0585 \times T)} \tag{5}$$

where

RH = relative humidity,
T = temperature, °C, and
D = dew point, °C.

Over the range of values observed in this study, Eq 5 gives the relative humidity within ±1 percent, which is probably lost in the error caused by the use of inaccurate dew-point data.

This equation and the hourly average data for temperature and dew point were used to calculate hourly average relative humidity. If the dew point exceeded the temperature or data were missing, the relative humidity was assumed to be 100 and flagged. For flagged relative humidities, the averages of relative humidities at the other three sites were calculated. If the average was equal to or greater than 85, the value was kept at 100. If the average was less than 85, the average replaced the 100. This procedure (1) gives values for missing data, (2) counteracts bias from the validation process, and (3) tends to normalize the data. It probably creates a lot of hourly averages of 100 which actually are within the range of 95 to 100.

Figure 2 is a comparison of the results between sites and with data from the National Weather Service Office at the St. Louis International Airport during the same period of exposure. The airport data are single observations at 3-h intervals. The number of observations is multiplied by three for comparison. Also shown is the number of hours at RH = 100 percent.

The behavior below 60 percent is relatively consistent. With the exception of Site 122 the hours at 100 percent are consistent. Site 122 had the least missing data and the highest number of values within the range of 95 to 100 percent. Other variations from site to site may be real or caused by dew-point error.

An analysis of variance of the relative humidity data showed that the vari-

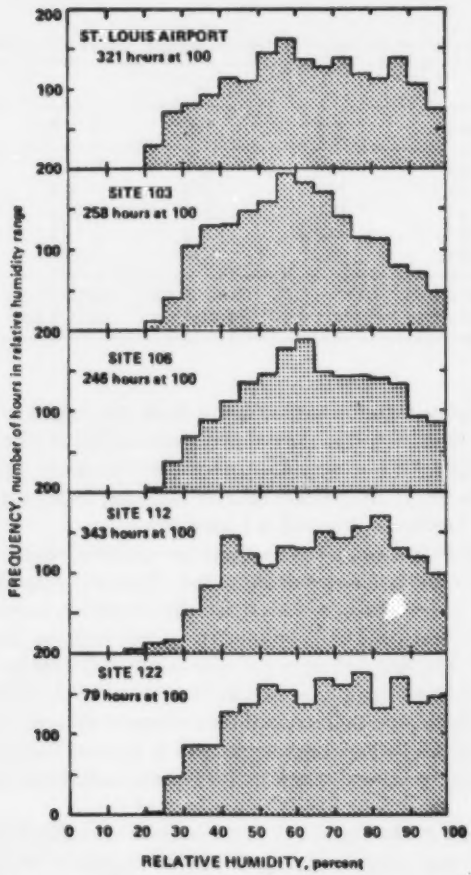

FIG. 2—*Comparison of relative humidity distributions in St. Louis.*

ables of site, day, and hour were all highly significant in increasing order. This type of behavior is expected and tends to validate the data.

In estimating time-of-wetness it is useful to know the fraction of time that some critical relative humidity is exceeded. Table 5 presents this type of data for the four sites and the airport. Also given are linear regression coefficients for each set of data.

These results and the percent-of-time-when-wet values from Table 4 can be used to estimate critical relative humidities. The respective critical relative humidities thus calculated for Sites 103, 106, 112, and 122, are 90, 91, 89, and 85. The overall best estimate of the standard deviation on each value is 0.8.

TABLE 5—*Percent of time stated relative humidity was equaled or exceeded.*

	Site				
RH	Airport	103	106	112	122
100	15.6	12.2	11.6	16.2	3.7
95	19.0	14.6	15.8	20.9	10.7
90	24.1	18.0	20.4	26.5	17.3
85	30.1	21.8	26.8	32.6	25.4
80	35.6	27.2	33.4	40.7	31.6
Intercept	116.86 ± 5.05	85.72 ± 5.72	119.88 ± 5.94	136.64 ± 6.58	144.64 ± 2.61
Slope	−1.02 ± 0.06	−0.74 ± 0.06	−1.09 ± 0.07	−1.21 ± 0.07	−1.41 ± 0.03

The only site that is significantly different from the others is Site 122. The critical relative humidities for the copper/steel ACM's at Sites 112 and 122 should be the same. This observed behavior and the significant difference in the number of hours at 100 percent relative humidity indicate that the upper end of the distribution at Site 122 is biased low.

The data in Tables 4 and 5 have a common variable, which is the percent of time a stated value is equaled or exceeded. Thus, any selected critical corrosion rate can be related to a critical relative humidity. Linear regressions were obtained for each site and comparisons were made for statistical differences. Sites 103, 106, and 112 were not statistically different but Site 122 was different from the others. This is demonstrated in Fig. 3, which shows that the 95 percent confidence limits on the true means of critical relative humidities mutually exclude the two regression lines. It appears that calculated relative humidities in the critical range at Site 122 are biased low by more than 5 percent.

Over 99 percent of the variability in the relative humidity frequency distributions for all sites shown in Fig. 2 can be explained by the empirical relationship

$$f = e^{-4.6[100-RH_{crit}/RH_{avg}][RH/100)^3} \quad (6)$$

where f is the fraction of time that relative humidity equals or exceeds the stated value and RH_{avg} is the average relative humidity.

This equation can be used to estimate the fraction of time a surface is wet if the critical relative humidity and the average relative humidity are known. Conversely, the average relative humidity can be estimated if the fraction of time when wet and critical relative humidity, as represented by RH in Eq 6, are known. Table 6 is a comparison of values calculated from data in Table 4 assuming a critical relative humidity of 90 percent with average of calculated data shown in Fig. 2.

Within the same air mass, one would expect the average relative humidity to be inversely related to average temperature from site to site in a functional

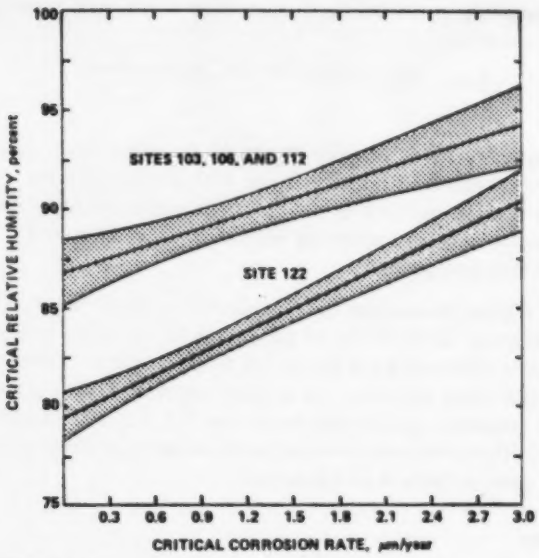

FIG. 3—*Comparison of critical relationships for assumed wetness.*

relationship similar to Eq 5. Some moisture may be gained or lost as the temperature changes, so the change in dew point will not be as large as the temperature change. Thus, the change in the temperature/dew-point spread will only be a fraction of the temperature difference.

Based on the airport average values of relative humidity (68.38), temperature (9.52°C), and dew point (2.92°C), the constant in Eq 5 is −5.05 rather than −6.32 as it is for the point-in-time relationship. As an approximation, the change in the average temperature/dew-point difference from site to site is assumed to be one third of the average temperature change from site to site. The average temperatures at Sites 103, 106, 112, and 122 were, respectively, 10.45, 10.89, 10.67, and 8.31°C. These values, the airport data, and the fol-

TABLE 6—*Comparison of average relative humidities using different methods.*

Site	From Dew-Point Data	From Fraction of Time When Wet[a]
Airport	68.38	. . .
103	65.38	66.47
106	68.78	68.04
112	71.76	72.60
122	67.65	70.95

[a] Assumed to be wet when corrosion rate of 1.5 μm/year was exceeded.

lowing expression derived from Eq 5 can be used to estimate average relative humidities at each site

$$RH_i = RH_0 e^{-5.05[80-2T_0+3D_0][T_i-T_0]/3(80+T_i)(80+T_0)} \quad (7)$$

where

RH_i = average relative humidity at site with missing dew-point data,
RH_0 = average relative humidity at site with dew-point data,
T_i = average temperature at site with missing dew-point data,
T_0 = average temperature at site with dew-point data, and
D_0 = average dew point.

The average relative humidities thus estimated for Sites 103, 106, 112, and 122 are, respectively, 67.46, 67.04, 67.25, and 69.62. From Eq 6 the respective fractions of time when wet are 0.198, 0.192, 0.195, and 0.231. With the exception of Site 112, these estimates are in good agreement with the data from Table 4. The respective percentage errors are 7.7, 7.2, 30.9, and 8.8 with a median of 7.7. This compares favorably with an average two-standard deviations on the data in Table 4 of 3.9 percent.

Pollution Data

With the exception of Site 112, the following gaseous pollutants were continually measured and recorded: O_3, NO, NO_2, CO, CH_4, SO_2, H_2S, total nitrogen oxides, total hydrocarbons, and total sulfur-containing gases. Site 112 did not measure SO_2 and H_2S but did measure the others. All of the data were expressed in parts per million. Details on instrument accuracy, calibration procedures, and data validation are given in Ref *1*.

Among several validation procedures was a correction for data with values below the lower detectable limit for each instrument. The measured value was replaced by one half of the lower detectable limit. Values were quite often in this range. This procedure excludes many values caused by low-side instrument error while keeping the high-side values, thus tending to bias long-term low-level averages toward the high side.

From the results of previous experiments and theoretical considerations, there is no reason to believe that hydrocarbons significantly affect corrosion rate. With both hydrocarbons and oxides of nitrogen primarily emissions from mobile sources, they are expected to be highly covariant. Other groups of pollutants are covariant, for example, NO, NO_2, and total oxides of nitrogen. Three of the pollutant measurements were selected for detailed analysis: O_3, total nitrogen oxides, and total sulfur. The last two can serve as proxies for their related compounds.

The hourly average ppm-values for these gases were converted to micrograms per cubic metre ($\mu g/m^3$) using the perfect gas law, assuming one atmosphere pressure and the average temperature during each measurement. Total nitrogen oxides were expressed as nitrogen dioxide and total sulfur as sulfur dioxide.

The lower detectable limit for each of these instruments was 0.005 ppm. Many hourly average values were recorded as 0.0025 ppm, especially for ozone and total sulfur. This converts to less than 10 $\mu g/m^3$. When long-term averages are around 30 $\mu g/m^3$, however, these low-level values become a significant part of the average.

The ACM's can respond only to the pollutants that reach their surfaces. For that reason pollutant flux should be a more important factor than pollutant concentration. Each of the pollutant concentration values was multiplied by the deposition velocity calculated from wind speed to give values for flux. The resulting averages for the total exposure time are given in Table 7.

Both NO_2 and SO_2 can react with zinc to form soluble products. The flux values in Table 7 can be multiplied by 0.0314 and 0.045 for NO_2 and SO_2 stoichiometric reactions, respectively, to calculate equivalent zinc corrosion rates that can possibly be caused by these pollutants. For NO_2 at Sites 103 and 106 the rates are 2.25 and 2.53 μm/year, respectively. Similarly for SO_2 the respective values are 1.26 and 1.23 μm/year. In total these corrosion rates exceed the average corrosion rates calculated from weight loss data or from the ACM responses. This suggests that not all of the pollutants that can reach the zinc surface react to form a soluble product. The formation of a sulfate is thermodynamically favored over the formation of a nitrate. When the SO_2 level is low and the NO_2 level high, however, the less-favored reaction can occur.

For a subset of data where relative humidity was equal to or greater than 95 and the ACM's corrosion rate was equal to or greater than 3 μm/year (surfaces most probably wet), the average flux of SO_2 was considerably lower than for the total time. The total possible contribution of SO_2 was considerably lower than for the total time. The total possible contribution of SO_2 and NO_2 pollutants during the periods of wetness was 2.95 μm/year for zinc. This value is considerably smaller than the average corrosion rate of 13.83 μm/year that was measured with the ACM's during the same periods. It is possible, thus, that some of the pollutant that is absorbed during dry periods reacts with the surface when it is wet.

Analysis of Relationships

The obvious relationship between ACM response and relative humidity is evidenced by Fig. 4. Both the timing of peaks and their magnitudes are shown to be related. This strong effect and the magnitude of error in the relative humidity make analysis for the possible effects of other variables difficult. The technique of multiple-regression analysis assumes that the independent variables are fixed (error-free) and are independent of each other (not covariant). Relative humidity was the least accurate of the "independent" variables. Thus, its error can mask the possible effects of other variables.

The use of a correlation matrix can reveal the problem of covariance between "independent" variables. A matrix for data at the four sites is given in Table 8.

TABLE 7—*Averages for pollutants at each site.*

Site	O_3		NO_2		SO_2	
	Concentration, $\mu g/m^3$	Flux, $\frac{cm}{s} \cdot \frac{\mu g}{m^3}$	Concentration, $\mu g/m^3$	Flux, $\frac{cm}{s} \cdot \frac{\mu g}{m^3}$	Concentration, $\mu g/m^3$	Flux, $\frac{cm}{s} \cdot \frac{\mu g}{m^3}$
103	41.9	34.3	115.5	71.8	34.4	28.0
106	31.9	21.0	148.3	80.6	48.7	27.4
112	30.4	20.3	136.9	65.3	17.8	10.3
122	51.2	28.6	28.0	15.1	47.1	23.9

NOTE: Flux is the product of deposition velocity (u), cm/s, and concentration, $\mu g/m^3$. Multiply by 31.5 to get $\mu g/cm^2$ year.

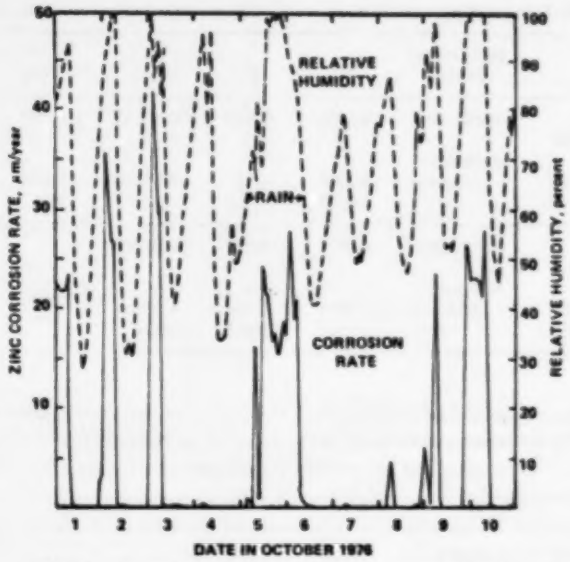

FIG. 4—*Atmospheric Corrosion Monitor response at Site 106.*

Only the temperature factor (E) and SO_2 concentration correlation coefficient were not included at this level of significance. As expected, relative humidity is the variable most significantly correlated with the logarithm of corrosion rate. It in turn is significantly correlated with all the other variables. Multiple-regression analysis of such data can produce equations with statistically significant coefficients. The magnitudes of those coefficients, however, may have little relationship to cause and effect.

Table 9 gives the results of multiple-regression analysis of zinc and steel ACM sets of data.

TABLE 8—*Correlation matrix of variables for four sites.*

Variable	Correlation Coefficients for Variable Pairs Which Exceed 0.999 Probability of Significance					
	RH	E	u	SO_2	NO_2	O_3
LnC	0.72	0.07	−0.21	−0.10	0.12	−0.23
RH	. . .	0.36	−0.20	−0.06	0.16	−0.36
E	. . .	. . .	−0.12	. . .	0.07	−0.40
U	. . .	. . .	. . .	−0.10	−0.27	0.34
SO_2	. . .	. . .	. . .	. . .	0.08	−0.05
NO_2	. . .	. . .	. . .	. . .	. . .	−0.28

NOTE: C = corrosion rate, μm/year; other terms defined in text.

TABLE 9—*Multiple-regression analysis results for logarithm of corrosion rate.*

	Independent Variable	RH	E	$u \cdot SO_2$	$u \cdot NO_2$	Constant
Zinc	coefficient	0.1000	−5.460	−0.00150	0.00493	9.9242
N = 2974						
	standard					
R^2 = 0.560	deviation	0.0017	0.323	0.00056	0.00051	
F = 943.7	F	3462.2	286.0	7.0	93.5	. . .
Steel	coefficient	0.0951	−6.299	−0.01307		15.3703
N = 2074						
	standard					
R^2 = 0.606	deviation	0.0018	0.364	0.00203		
F = 1061.8	F	2736.6	299.3	41.4		. . .

With the exception of the SO_2 flux, the signs for the coefficients are as expected. The negative covariance between relative humidity and SO_2 concentration may be causing the negatively significant coefficient for the SO_2 flux. The actual values for the coefficients for relative humidity and E are probably higher than the foregoing results because of their counteracting nature and their strong covariance.

When the surface of the ACM is completely wet, the ambient relative humidity should have no effect on the corrosion rate. It was assumed that when the corrosion rate was equal to or greater than 3.0 μm/year and the ambient relative humidity was equal to or greater than 95 percent, the surfaces should be completely wet. Table 10 gives the correlation matrices and results of multiple-regression analysis of these subsets of data.

The signs for the temperature factor coefficients and the NO_2 flux are as expected. The unexpected negative sign for the deposition velocity (μ) effect and the negative correlation between u and NO_2 for the zinc ACM data indicate that the deposition velocity is acting as a proxy for the NO_2. Comparing the magnitudes of the temperature factor coefficients with those of Table 9 shows that for zinc the value is lower and for steel it is higher. It was expected to be higher in both cases because the effect of relative humidity was not present to counteract it.

The correlation between temperature factor and SO_2 in the case of the zinc data could explain the observed lack of statistical significance for pollutants. The temperature factor has a negative effect, which may be partially offset by a positive SO_2 effect and a positive NO_2 effect. For the steel data the covariance between the temperature factor and NO_2 can reduce the magnitude of both coefficients.

The data were further restricted to the range of temperature factors where $3.46 \leq E \leq 3.50$ to see if the pollutant effects were significant. Corrosion rate rather than the logarithm of the corrosion rate was taken as the dependent variable. Even with this restriction there was still a strong correlation between

TABLE 10—*Results of analysis of wet surface data.*

Zinc ACM's

	Correlation Coefficient Matrix for Variable Pairs[a]				
	E	*u*	SO_2	NO_2	O_3
LnC	−0.38	−0.21	. . .	. . .	. . .
E	. . .	. . .	0.23	0.32	. . .
u	. . .	. . .	. . .	−0.48	. . .
SO_2	. . .	. . .	. . .	0.21	. . .
NO_2	. . .	. . .	. . .	. . .	. . .

Regression Equation			
Variable	Coefficient	Standard Deviation	*F*
Constant	15.0778		
E	−3.428	0.495	48.0
u	−0.4658	0.1115	17.4
$N = 277, R^2 = 0.1869, F = 31.5$			

Steel ACM's

	E	*u*	SO_2	NO_2	O_3
LnC	−0.48	. . .	−0.18	. . .	. . .
E	. . .	. . .	. . .	0.19	. . .
u	. . .	. . .	−0.27	−0.30	. . .
SO_2	. . .	. . .	. . .	−0.19	0.21
NO_2	. . .	. . .	. . .	. . .	−0.3

Variable	Coefficient	Standard Deviation	*F*
Constant	35.6164		
E	−9.134	0.836	119.4
$u \cdot NO_2$	0.00246	0.0008	9.5
$N = 375, R^2 = 0.249, F = 61.0$			

[a]Significant at 0.999 probability.

the temperature factor and O_3 for the steel data, with a positive correlation between O_3 and SO_2. This resulted in significant negative coefficients for SO_2 and O_3 flux. Table 11 is a correlation matrix for the zinc ACM subset. The zinc corrosion rate is significantly correlated with SO_2 and NO_2 concentrations and fluxes. The coefficients for fluxes are higher than for concentrations. The temperature factor correlates only with NO_2 concentration and not with NO_2 flux.

Regression analysis results are given in Table 12. Both of the coefficients in Table 12 are higher but not significantly different from coefficients predicted from stoichiometric reactions: 0.045 for $u \cdot SO_2$ and 0.0314 for $u \cdot NO_2$. This is possibly caused by the absorption of some of the pollutants reaching the surface when it is dry and then reacting when it is wet. Another possibility is that the total concentration of these pollutants in the atmosphere was higher than was measured by the instruments that measure only gases.

From Table 7, the average fluxes at the zinc ACM sites during the total exposure

$$\left(27.7 \frac{\text{cm}}{\text{s}} \cdot \frac{\mu\text{g}}{\text{m}^3} \text{ for } u \cdot SO_2 \text{ and } 76.2 \frac{\text{cm}}{\text{s}} \cdot \frac{\mu\text{g}}{\text{m}^3} \text{ for } u \cdot NO_2\right)$$

are considerably higher than the mean fluxes (Table 12) during the periods of wetness and restricted range of temperatures. The pollutants don't just disappear during periods of high relative humidity. They are absorbed into condensed moisture in the atmosphere as well as on surfaces. Some may be catalyzed in solution to sulfuric and nitric acid. The pollutants, though still in the atmosphere, can no longer be measured as a gas. The unmeasured pollutants still can contribute to corrosion by being delivered to the surfaces by the flux of moisture particles.

If it is assumed that the actual fluxes of pollutants during periods of wetness were higher than measured by the ratio of the total time average to the average during periods of wetness, the calculated damage coefficients are lower: 0.052 for $u \cdot SO_2$ and 0.054 for $u \cdot NO_2$. These values are quite close to the theoretically predicted coefficients for stoichiometric reactions.

While a previous study [*5*] provided evidence for the stoichiometric reac-

TABLE 11—*Correlation matrix for zinc ACM's within restricted temperature range when wet.*

	Correlation Coefficient[a]/Number of Sets							
	E	u	SO_2	NO_2	O_3	$u \cdot SO_2$	$u \cdot NO_2$	$u \cdot O_3$
C	. . .	. . .	0.18/98	0.28/99		0.27/98	0.37	. . .
E	. . .	. . .	. . .	0.21/99		. . .	. . .	. . .
u	. . .	. . .	. . .	−0.46/97		. . .	. . .	. . .
$u \cdot NO_2$	. . .	. . .	. . .	. . .	. . .	. . .	. . .	−0.27/87

[a]Significant at 0.95 probability level; fluxes include u in term.

TABLE 12—*Regression analysis of zinc ACM subset of data.*

Variable	Constant	$u \cdot SO_2$	$u \cdot NO_2$	$N = 77$
Mean	μm/year	$10.6 \frac{cm}{s} \cdot \frac{\mu g}{m^3}$	$60.3 \frac{cm}{s} \cdot \frac{\mu g}{m^3}$	
Coefficient	14.14	0.13	0.06	$R^2 = 0.1766$
Standard deviation	. . .	±0.076	±0.02	$F = 7.936$
F	. . .	3.2	12.3	

tion of SO_2 with zinc, this is the first evidence for NO_2 in the atmosphere reacting with zinc. Previous data sets were too small to partition into meaningful-size subsets that eliminate covariance of "independent" variables. Even with this large data set it was not possible to eliminate the covariance between temperature and pollutants at the steel ASM sites. Thus, the coefficient for the temperature effect includes by proxy the effects of pollutants.

A technique of fixing the coefficients as determined in the absence of covariance, and calculating the coefficient for the remaining variable for data sets where that variable was covariant with the others, was used to determine an overall relationship for the zinc/copper ACM's. This was a two-step process involving increasingly larger data sets. First, a temperature factor coefficient and intercept were calculated on those data where the corrosion rate equaled or exceeded 3 μm/year and the relative humidity equaled or exceeded 95 percent. Second, a coefficient for the effect of relative humidity was calculated using the complete data set. It was assumed that the maximum amount of corrosion occurs at 100 percent relative humidity and follows the functional form

$$C = Cm\, e^{-R(100-RH)/RH} \tag{8}$$

where *C* is the corrosion rate and *Cm* the maximum corrosion rate (function of temperature and pollution level). Based on the results of this technique and stoichiometric reactions with pollutants, the best estimates of coefficients produce the relationship

$$Co = [0.045\, u \cdot SO_4 + 0.0314\, u \cdot NO_2 + e^{17.133-4.237E}]e^{-5.4(100-RH)/RH} \tag{9}$$

where *Co* is the best estimate of the corrosion rate μm/year for specific conditions of pollutants, temperature, and relative humidity.

This equation can explain approximately 43 percent of the observed variability in the zinc corrosion response. Relative humidity accounts for 35.1 percent, temperature 6.6 percent, and the pollutants only 1.3 percent of the total variability. The standard deviation on *Co* is 5.5 μm/year. Because conditions at the surface of the ACM lead or lag ambient conditions and the ambient relative humidity values have considerable error, a much better fit is not expected. For example, at average levels of pollutants and temperature,

an error of 5 percent relative humidity can cause an error in *Co* of around +2.8 μm/year. At the higher observed temperatures the same error in relative humidity can cause a +7.9-μm/year error in the estimated corrosion rate.

Coupling the zinc to copper accelerates the corrosion of the zinc. Only the constant (17.133) in the temperature exponential term is involved in this effect. From the data in Tables 2 and 4 the constant for uncoupled zinc was calculated to be 12.897. Thus, an equation for the instantaneus corrosion rate of zinc as a function of pollutants, relative humidity, and temperature is

$$Co = [0.045\ u \cdot SO_2 + 0.0314\ u \cdot NO_2 + e^{12.897 - 4.237E}]e^{-5.4(100-RH)/RH} \quad (10)$$

When the surface is fully wet at a temperature of 11°C and an NO_2 flux of 36 (cm/s · μg/m^3), the equation simplifies to

$$Co = 1.264 + 0.045\ u \cdot SO_2 \quad (11)$$

This equation is very close to the results of a regression of weight loss data for small galvanized specimens exposed at the average conditions of 11°C and 36 (cm/s · μg/m^3) for NO_2 flux [*5*]

$$\frac{C_z}{tw} = 2.32 + 0.049\ u \cdot SO_2 \quad (12)$$

where C_z is the corrosion in micrometres and *tw* the time-of-wetness in years.

The covariance between the pollutants and the temperature factor makes it impossible to calculate meaningful pollution coefficients for the steel/copper ACM's exposed at Sites 112 and 122. The temperature factor effect includes by proxy the effects of the pollutants. The best estimate of a relationship for the steel ACM's is

$$Co_s = e^{33.583 - 8.778E - 6.89(100-RH)/RH} \quad (13)$$

TABLE 13—*Mean and standard deviations of pollutant variables.*[a]

Variable	Units	Mean	Standard Deviation
Deposition Velocity *u*	$\frac{cm}{s}$	0.5399	0.1968
SO_2	$\frac{\mu g}{m^3}$	36.61	33.29
NO_2	$\frac{\mu g}{m^3}$	61.44	121.53
O_3	$\frac{\mu g}{m^3}$	44.01	38.25
$u \cdot SO_2$	$\frac{cm}{s} \cdot \frac{\mu g}{m^3}$	18.90	19.13
$u \cdot NO_2$	$\frac{cm}{s} \cdot \frac{\mu g}{m^3}$	29.23	51.23
$u \cdot O_3$	$\frac{cm}{s} \cdot \frac{\mu g}{m^3}$	25.54	25.65

[a] Based on 2074 sets of data from Sites 112 and 122.

where Co_s is the best estimate of the instantaneous corrosion rate for steel in μm/year at particular values of E and relative humidity.

The constants 33.585 and −8.778 include the effects of pollutants as well as temperature at these two sites. The equation is not applicable to other locations if the pollution levels are not similar. As a point of reference, Table 13 gives the means and standard deviations for the variables that could be affecting the corrosion rate.

Summary and Conclusions

The Atmospheric Corrosion Monitors developed and used by Mansfeld and co-workers can be used to indicate the magnitude of corrosivity as well as time-of-wetness. The response of the ACM's to changes in ambient conditions, however, is affected by their geometry. Couples mounted on a very thin substrate should respond faster to such changes. Over long averaging times the errors caused by leads and lags in response will tend to compensate each other and reduce the total error. Total time-of-wetness measured by this device should be representative of the time-of-wetness on most metal surfaces.

A galvanic current equivalent to a corrosion rate equal to or greater than 1.5 μm/year appears to be a good criterion for assuming that the ACM surface is wet. This value corresponds to a critical relative humidity of approximately 90 percent. From 88 to 99 percent of the corrosion measured at the four sites occurred when values met this criterion.

Corrosion rates are strongly dependent on relative humidity; however, relative humidity is one of the least accurate environmental measurements. It is seldom measured where materials are exposed, yet microclimate differences can be significant between sites that are within a few hundred metres from each other. Because temperature and relative humidity are related to each other within the same air mass, an unknown relative humidity can be estimated from temperature differences and a relative humidity at a different site. With average relative humidity, time-of-wetness can be estimated.

In the real world, environmental factors are strongly covariant and subject to error. The unquestioned use of multiple-regression analysis of such data to explain corrosion behavior can be misleading. A large data set collected in St. Louis allowed partitioning into subsets that eliminated covariance. Through this process it was determined that the flux to the surface of total oxides of nitrogen (expressed as NO_2) as well as the flux to the surface of total sulfur (as SO_2) contributed significantly to the corrosion response of zinc/copper ACM's. This is the first time an NO_2 effect has been observed in a field experiment.

Covariance of pollutant fluxes with temperature made it impossible to delineate pollutant effects on the steel/zinc ACM's. For both the zinc and the steel ACM's, temperature and relative humidity affected corrosion rate in increasing order of significance. With relative humidity the most important

factor, and being most in error, the empirical expressions relating corrosion rate to environmental factors are as good as one can expect. The resulting expression for zinc corrosion agrees well with expressions derived from other data.

Acknowledgments

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Mr. William Deland of Computer Sciences Corp. spent many hours in programming so that the data could be analyzed as they were. It required much more than creating a data file to be analyzed by standard statistical programs. The procedures that were finally used evolved as work proceeded, based in part on trial and error of theoretical considerations. Without Mr. Deland's ability and patience I would not have been able to complete this work.

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